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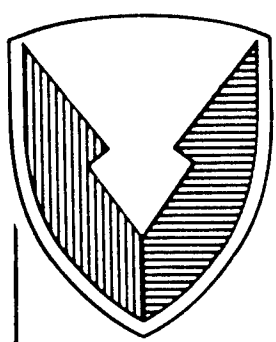
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Technical Report

No. DAAG29-85-K-0225

Improved Adhesion Performance of Polyamid
Fibers In Fiber-Reinforced Composites

By Dr. Jack L. Koenig

Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

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Improved Adhesion Performance of Polyamid
Fibers in Fiber-Reinforced Composites

Final Report

Authors:

Dr. Jack L. Koenig and Shari L. Tidrick

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1.0 Introduction

The high tensile properties of composites reinforced by poly-p-phenylene terephthalamide fibers (PPTA), sold under the trade name of Kevlar by Du Pont, are well known. However, the transverse properties are relatively low compared to composites utilizing other high modulus fibers. This has been attributed to poor adhesion between the fiber and the matrix, as evidenced by the observation of splitting and bare fibers at the fracture surfaces¹. According to Penn, Bystry, Karp and Lee², the three main adhesion mechanisms include intermolecular interactions (2-6 kcal), primary chemical bonds (60-100 kcal), and mechanical interlocking (variable). Several methods can be used to attempt to improve Kevlar fiber-matrix adhesion, including the use of coupling agents or coatings³⁻⁸, grafting⁹⁻¹⁰ and modification of surface functionalities through plasma treatments¹¹⁻¹⁴ or wet chemical methods^{10,14-18}. Because many of Kevlar's most demanding and critical applications are reinforcement in epoxy matrices, much of the work cited above has attempted to increase Kevlar/epoxy adhesion; however, these techniques may be used for any matrix material.

Modification of surface functionalities offers the greatest improvements in properties, since successful improvement has been limited for grafting and the use of coupling agents or coatings. Plasma treatments can effectively introduce surface functionalities, but offer several disadvantages, including surface oxidation¹² loss of tensile strength of individual fibers¹³, chain scission and ablation (weight loss)¹⁹. The high degree of chemical inertness of Kevlar precludes the use of most wet chemical methods; however, the metalation reaction on PPTA is quite well documented^{10,15-17}. The proposed reaction scheme is shown in Figure 1¹⁶.

According to Takayanagi and Katayose¹⁹, the following reactions have been performed on metalated PPTA in powder form: N-propylation, N-butylation, N-heptylation, N-dodecylation, N-octadecylation, N-benzylation, N-(1-naphtyl)methylation, N-(9-anthyl)methylation and N-carboxymethylation. Takayangi, et. al.^{15,16} reports reacting metalated Kevlar fibers with various compounds, including bromoacetic acid, epichlorohydrin, acrylonitrile phenyl glycidial ether and a bisphenol-A-based epoxy.

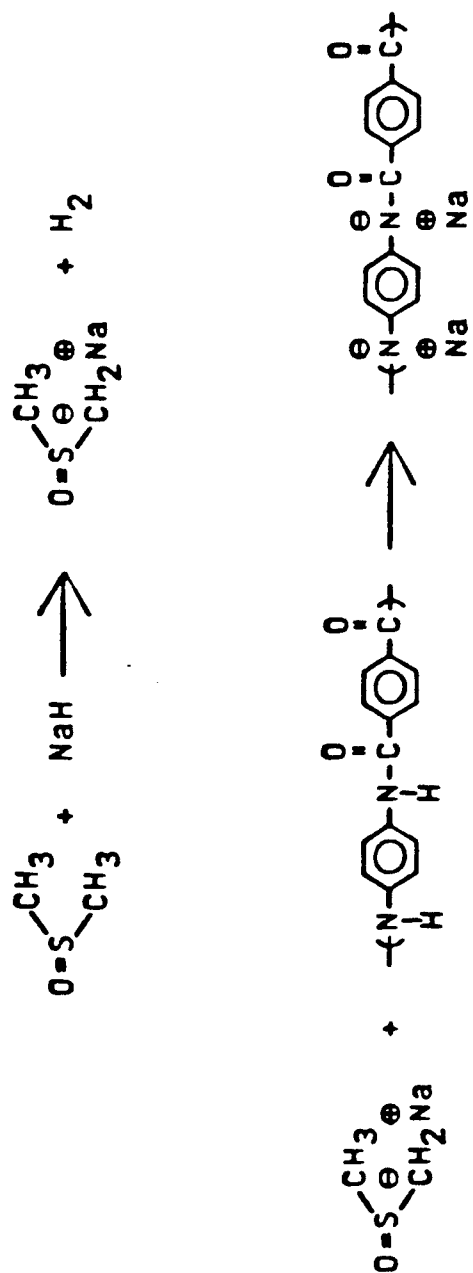


Figure 1. Proposed reaction scheme for the metalation of poly-(p-phenylene terephthalamide).

Another problem involved with surface modification of fibers is characterizing the surface reaction, since small changes (approximately 1%) occur compared to the much larger bulk properties. Fourier-transform infrared (FTIR) spectroscopy is a powerful analytical method to use in characterizing the extent and products of reaction. A FTIR technique which has been gaining popularity in recent years is photoacoustic spectroscopy (PAS), which requires little or no sample preparation²⁰⁻²³. It is especially useful for highly reflective solid samples, such as Kevlar fibers^{24,25} which are difficult to investigate by other FTIR techniques. The sample is placed in a sealed, vibration-free chamber with a coupling gas such as helium, argon, or air. Modulated light is impinged on the sample, which selectively absorbs infrared light at those frequencies corresponding to molecular vibrations. This energy is then lost to the coupling gas through nonradiative processes as heat. The modulation of the incident light causes a periodic pressure fluctuation of the coupling gas in the chamber, which is detected by a sensitive microphone. The resulting signal can then be digitally converted to represent an absorbance spectrum. Increasing the modulation frequency enhances those absorbances due to the surface species

as opposed to bulk absorbances; however, increasing the modulation frequency also greatly increases the noise level of the resulting spectrum. Corrections must be made for the differences in depth of penetration at different wavelengths of the incident light²⁶. Also, many scans must be taken as the signal-to-noise ratio is quite low as compared to other FTIR techniques.

2.0 Experimental

The metalation and epoxidation reactions were performed in a glove bag at ambient temperatures under nitrogen atmosphere. Desiccant was placed in the glove bag to minimize moisture contamination. The metalation solution consisting of 150 ml dimethylsulfoxide (DMSO) and 0.07 g sodium hydride (NaH) was stirred for at least 4 hrs to ensure complete dissolution of the NaH. The reaction solution turned a very deep brown as the sodium methylsulfinylcarbanions were generated. Fiber lengths of approximately 75 cm of as-received Kevlar 49 fibers (courtesy of Du Pont), which had been dried at 120°C for 24 hrs, were metalated for periods ranging from 5 min to 24 hrs, then transferred directly into the epoxidation solution for a period of ten minutes. This solution consisted of a 75:25

mixture of DMSO:epichlorohydrin (ECH). The samples were then rinsed with acetone and dried under vacuum for 4 hrs before PAS analysis. All solvents were reagent grade or better. DMSO and acetone were obtained from Fisher Scientific, and the NaH and ECH were obtained from Aldrich.

Several samples which had been metalated for 10 min and then reacted in the DMSO/ECH mixture were boiled for 2 hrs, either in pure water or in a 5 wt % IR grade KBr (Aldrich) salt solution, and then dried at ambient temperature under vacuum for 48 hrs. Spectra were also obtained from boiled, wet fibers; however, interference due to the strong IR absorption of water prevented analysis.

All spectra were taken on a Digilab FTS-60 equipped with a He-Ne laser for frequency accuracy and purged with dried air from which the carbon dioxide had been removed. A Barnes PA cell was used. Two hundred and fifty scans of each sample was taken at a mirror speed of 0.15 cm/s, and depth penetration corrections were performed²⁶. Carbon black from Fisher Scientific which had been dried at 120°C for 24 hrs under vacuum was used as the reference. Samples were stored in a desiccator to avoid moisture contamination before analysis; all samples were

investigated within a period of 48 hrs of reaction. About 12.5 mg of Kevlar fibers were cut into 5 mm lengths and placed as nearly parallel as possible into the sample cup in order to avoid errors due to packing, sample volume, and orientation with respect to the IR beam²⁰.

3.0 Results and Discussion

The metalation reaction caused the bright yellow fibers to turn orange; the color was variable for samples reacted for short time periods, indicating that the reaction occurs inhomogeneously over the surface of the fibers. Fibers darkened as the metalation period was lengthened. The sodium methylsulfinylcarbanions should abstract available hydrogen from the amide groups on the surface of the Kevlar fibers instantaneously. Increased reaction time allows penetration into the more poorly organized fiber core, causing darkening of the fibers as degradation occurs. Takayanagi et al¹⁶ reported that fibers dissolve completely if metalated for a sufficient time period. The level of reaction for metalation periods of 2 hrs or less appeared to be at a constant level for a given treatment solution as opposed to increasing with treatment time, indicating that formation of the methyl sulfinylcarbanions was

incomplete even though all the NaH had dissolved. For metalation periods greater than 2 hrs, spectroscopic evidence indicates severe degradation of fiber structure. Subsequent reactions changed the fibers to their original bright yellow color. The spectrum of the reaction product yielded very intense peaks due to the treatment which were easily subtracted from an untreated sample after least-squares fitting.

The comparison of the transmission and PA peak frequencies for ECH, along with the assignments made by Kalasinsky and Wurrey²⁷ from a normal coordinate analysis study, are given in Table I. In the reaction spectrum (see figure 2) several new peaks appeared in the region 3100 to 2800 cm^{-1} which appear similar to the CH- stretching mode peaks that are present in ECH, but are shifted down several wavenumbers, presumably due to the conjugation and resonance which exists in Kevlar. Also, more -CH stretching mode peaks appear in the product spectrum than are seen in the ECH spectrum. Least-squares subtraction revealed a peak at 3335 cm^{-1} , attributed to a change in the NH-stretching modes. This peak may also, at least partially, be due to water absorption.

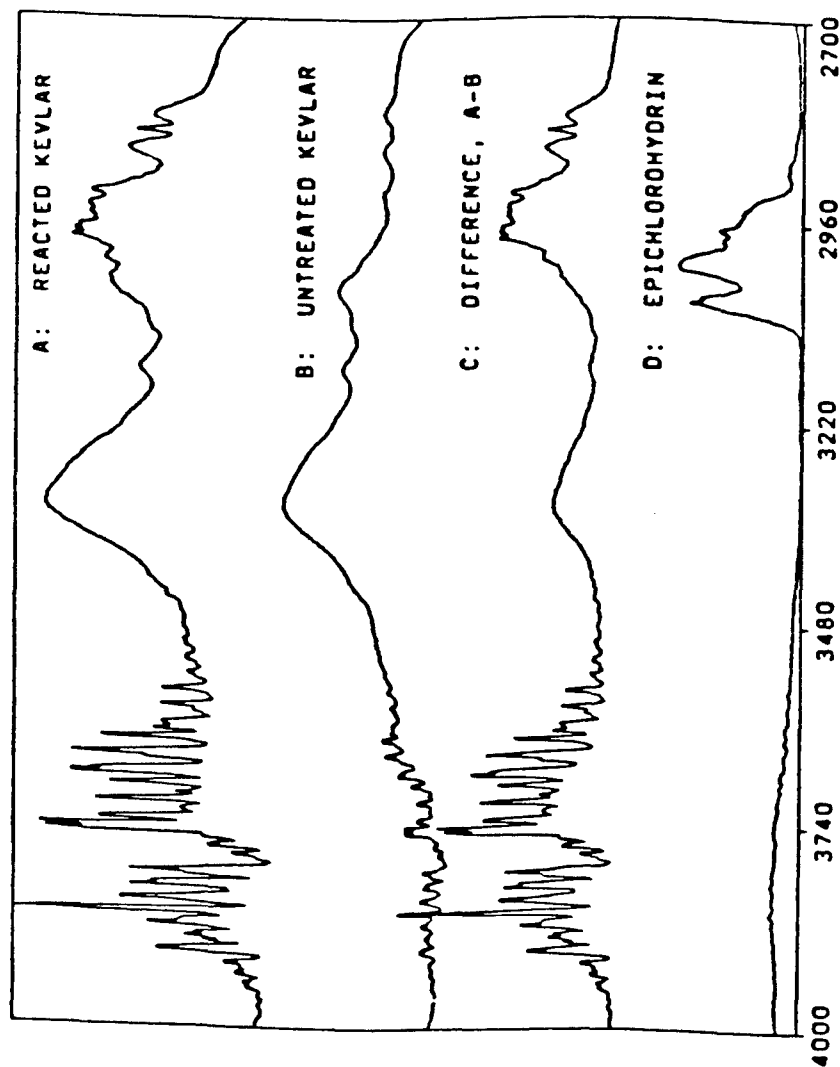


Figure 2. Photoacoustic FT-IR spectra of the region 4000-2700 cm⁻¹ of the following:
 A) Reacted Kevlar 49 fibers; B) As-received Kevlar 49 fibers; C) Difference, A-B; D) Liquid epichlorohydrin.

Several other spectroscopic changes are also observed. A triplet appears at 1055, 1034, and 1017 cm^{-1} (see Figure 3), similar to triplets which have been seen in many aromatic esters and acrylates²⁸. These peaks are quite intense and can be assigned to -CO- stretching modes. The peaks which are assigned to the ring modes in ECH²⁸ are absent from the reaction spectrum. The residual peaks at 897, 865, 863 and 789 cm^{-1} arise from shifts in the mixed modes due to C-N- stretching and ring deformation vibrations²⁹⁻³³. The 1800 to 1200 cm^{-1} region (see figure 4) indicates the presence of moisture in the reacted fibers. The absence of carbonyl stretching modes and the 1250 cm^{-1} peak which is characteristic of ethers²⁹ should be noted.

The spectroscopic evidence indicates the presence of one of the following: an epoxy, an ester, an ether, or a carboxylic acid. In order to distinguish among the various possibilities, samples which had been metalated for 10 min were boiled for 2 hrs, in pure water or in a 5% wt KBr solution.

Ethers are generally nonreactive. For all practical purposes, the ether linkages only undergo cleavage by acid. Cleavage takes place only under quite vigorous conditions, requiring the use of

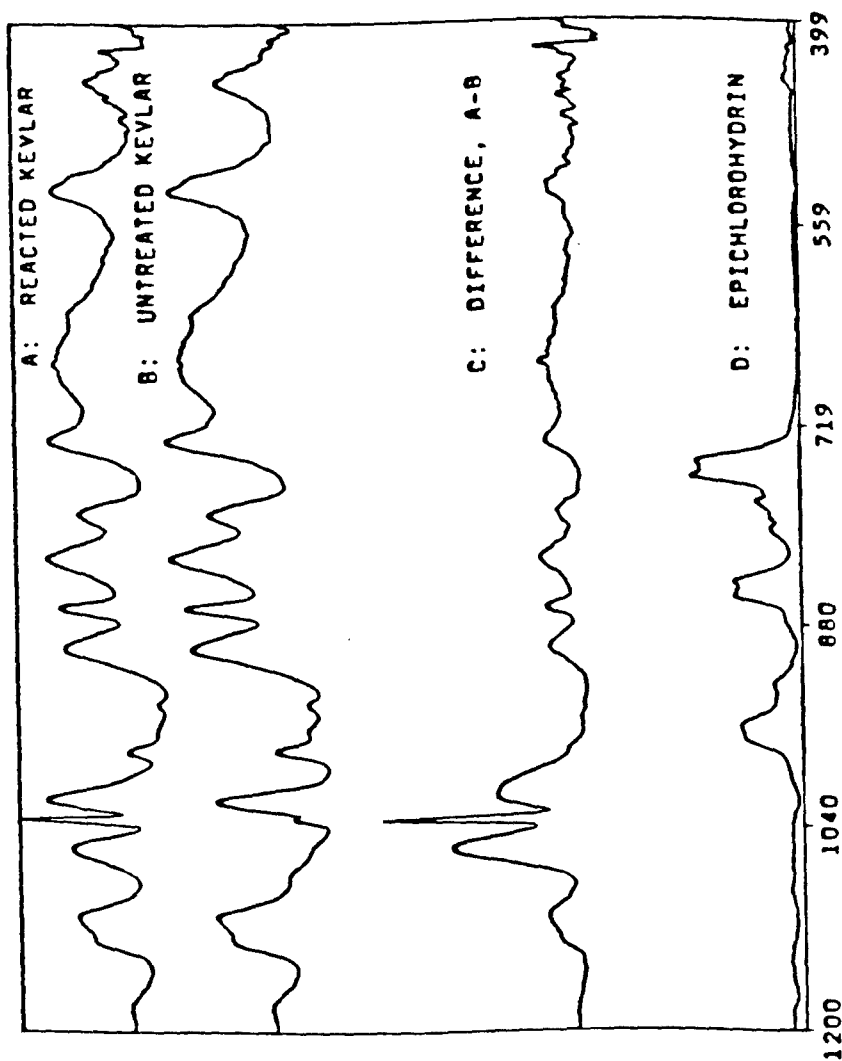


Figure 3. Photoacoustic₁ FT-IR spectra of the region 1200-400 cm⁻¹ of the following:
 A) Reacted Kevlar 49 fibers; B) As-received Kevlar 49 fibers; C) Difference, A-B; D) Liquid epichlorohydrin.

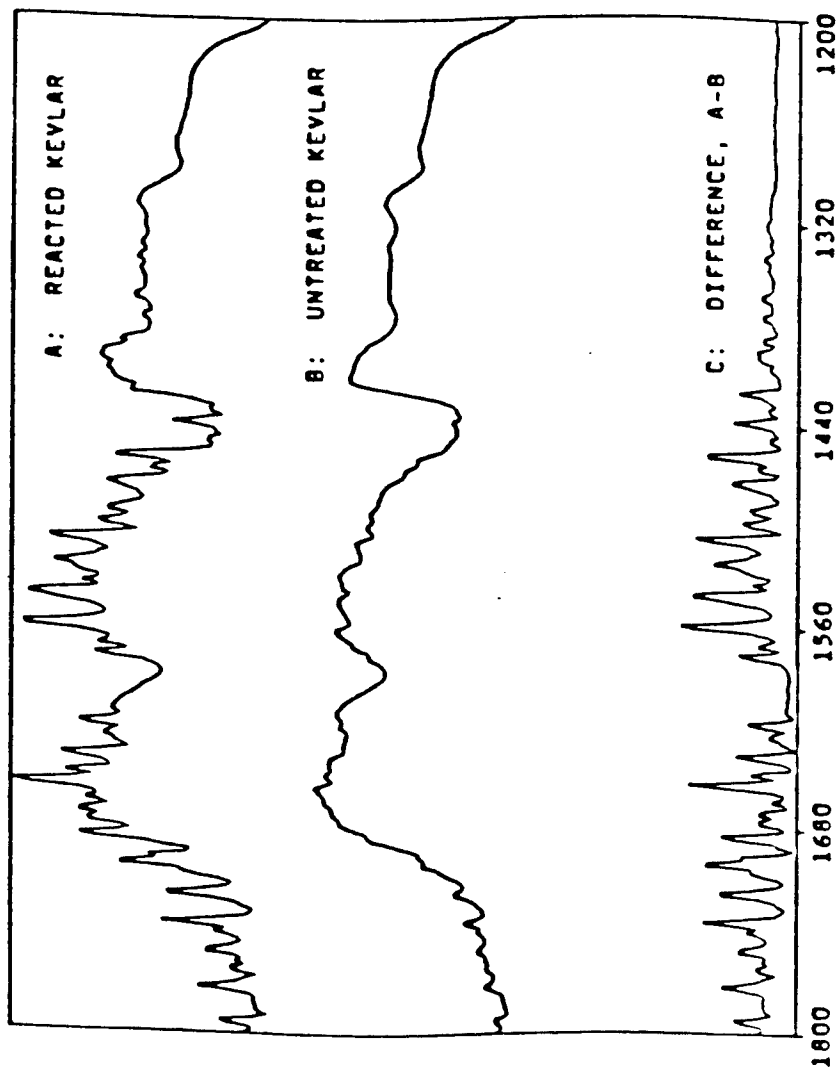


Figure 4. Photoacoustic FT-IR spectra of the region 1800-1200 cm^{-1} of the following:
 A) Reacted Kevlar 49 fibers; B) As-received Kevlar 49 fibers; C) Difference, A-B.

concentrated acids (usually HI or HBr) and high temperatures. Aromatic epoxides, on the other hand, are quite unstable and will cleave easily in the presence of acids, bases, or heat. A carboxylic acid would easily form a salt in boiling saline solution, resulting in large shifts in peak locations due to salt formation. Esters are in equilibrium with carboxylic acids, which could then form salts. However, it is doubtful that the reaction conditions are vigorous enough to destroy an aromatic ester. Figure 5 illustrates the reactions described above²⁹.

To summarize, then, ethers would give the same spectrum under the conditions investigated. Carboxylic acids should give the same spectrum after being boiled, but large shifts would occur after being boiled in saline solution. Esters are expected to yield a spectrum which is a combination of ethers and carboxylic acids, assuming that the reaction conditions are vigorous enough to yield an appreciable equilibrium concentration of the carboxylic acid. Hydrogen bonding peaks should appear if an alcohol had been formed from the epoxy. The experimental spectrum obtained was the same after each treatment, indicating the formation of an ether. The most likely mechanism that is supported by all the pertinent data is shown in figure 6.

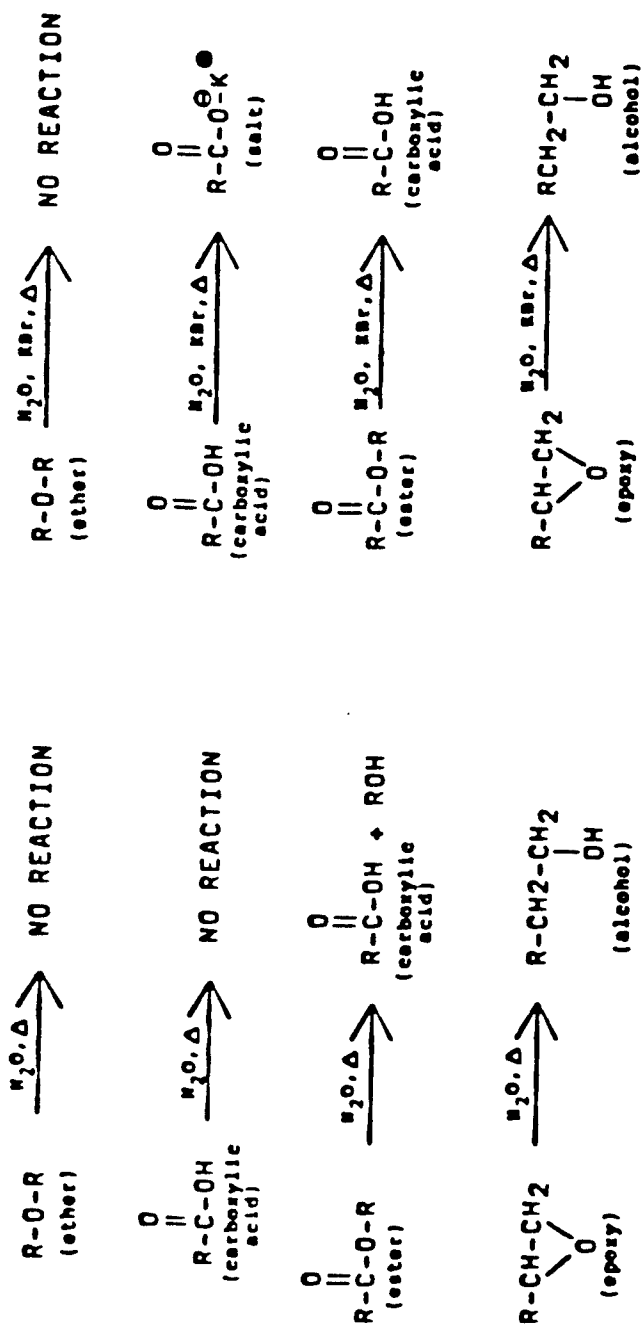
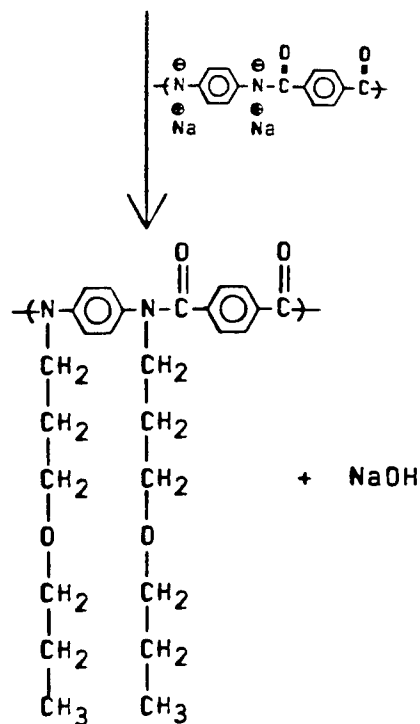
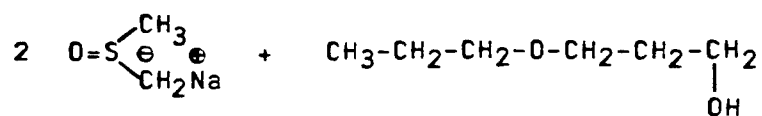
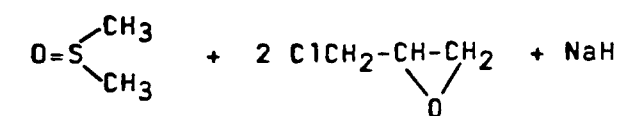


Figure 5. Schematic of the reactions that occur to the possible structures formed during the treatment when boiled in water or saline solution.



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This mechanism is also supported by the C/N and O/N ratios reported by Takayanagi, et al¹⁶. However, Penn and Larsen reported surface oxidation of the fibers³⁵. These groups could also react with the ECH, forming esters. Because the carbonyl modes due to the Kevlar structure absorb so strongly and broadly, any peaks attributed to surface oxidation are masked. Esters may also be stable under the boiling conditions described above, yielding the same spectrum for all treatments. However, the amount of surface oxidation is expected to be too small to give rise to the intense peaks observed for the reaction products.

4.0 Conclusions

PAS has been used to characterize the reaction products of metalated Kevlar and ECH. Several peaks appear which arise from the -CH stretching modes due to the addition of ECH to the fiber surface. The reaction product appears to be an unreactive ether, although ester formation is also possible. While primary bonds cannot form to promote adhesion, mechanical interlocking should result in some improvement of compressive properties. Mechanical testing is required in order to see if this procedure decreases the tensile strength of individual fibers. However, this study has demonstrated the utility of

FTIR-PAS as a viable method to characterize surface reactions of fibers.

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RECOMMENDATIONS

1. Due to the weakness of the adhesive bonding across the matrix-fiber interface, the surface character of Kevlar fibers must be improved to enhance the chemical bonding.

2. The chemical treatment must be delicate in order not to destroy the physical and mechanical properties of the Kevlar fibers.

3. The chemical treatment should result in the presence of active hydroxyl groups on the surface in order to initiate the polymerization of the epoxy matrix resulting in the largest numbers of interfacial bonds between the matrix and the fiber.

Table I. Vibrational Frequencies (cm^{-1}), Photoacoustic (PA) and Transmission (TR), and Assignments For Liquid Epichlorohydrin*

PA	TR	Assignment
3063 m	3065 m	ν_1 , CH_2 antisymmetric stretch
3017 ms	3005 s	ν_1 , CH_2 symmetric stretch
2968 m	2963 m	ν_3 , $\text{CH}_2(\text{Cl})$ antisymmetric stretch
2945 sh	2926 m	ν_5 , $\text{CH}_2(\text{Cl})$ symmetric stretch
1489 w	1480 m	ν_5 , $\text{CH}_2(\text{Cl})$ deformation
1456 w	1473 sh	ν_6 , gauche
1449 w	1446 m	ν_6 , CH_2 deformation
1418 w	1431 ms	ν_7 , gauche and cis
1406 w	1403 m	ν_7 , CH bend, in plane
1402 sh	1397 ms	ν_8 , gauche and cis
	1298 w	
1285 sh	1275 sh	ν_9 , gauche
1273 m	1264 vw	ν_9 , $\text{CH}_2(\text{Cl})$ wag
	1254 s	ν_{10} , ring breathing
1206 vw	1206 vw	ν_{10} , gauche
1191 vw	1191 w	ν_{11} , $\text{CH}_2(\text{Cl})$ twist
1145 vw	1145 sh	ν_{11} , CH_2 twist
1134 vw	1134 m	ν_{12} , gauche and ν_{14} , CH_2 wag
974 w	1090 mw	ν_{13} , CH bend, out of plane
961 ms	959 s	ν_{14} , gauche
928 ms	924 vs	ν_{15} , C-C stretch
858 ms	903 m	ν_{15} , $\text{CH}_2(\text{Cl})$ rock
847 ms	850 vvs	ν_{16} , antisymmetric ring deformation
		ν_{17}
804 w	840 sh	ν_{18} , symmetric ring deformation
793 sh		
781 m	788 mbd	ν_{19} , cis
762 vs	756 s	ν_{19} , CH_2 rock
748 vs	733 sh	ν_{19} , cis
	720 vvs	ν_{20} , C-Cl stretch
665 sh	692 mw	ν_{20} , gauche
	516 m	ν_{20} , gauche
443 w	441 s	ν_{21} , $\text{CH}_2(\text{Cl})$ bend, out of plane
		ν_{21}

* Abbreviations used are as follows: s, strong; m, medium; w, weak; v, very; bd, broad; sh, shoulder

PUBLICATIONS
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Determination of the Accessibility of N-H Groups of
Kevlar-49 Fibers by Photoacoustic FT-IR Spectroscopy

Fourier Transform Infrared Characterization of Chemically
Modified Kevlar 49 Surfaces

Photoacoustic FTIR Analysis of Surface-Modified Kevlar 49
Fibers

Morphology and Structure of Kevlar Fibers: A Review

Characterization of the Surface Hydrolysis of Kevlar-49
Fibers by Diffuse Reflectance FT-IR Spectroscopy

Application of a Modified FT-IR Photoacoustic Technique for
the Surface Characterization of Kevlar Fibers

An FT-IR Study of the Water Absorbed in Kevlar-49 Fibers

Characterization of Kevlar Fiber Surfaces Using a Newly
Developed Infrared Photoacoustic Technique

Determination of the Orientation of Adsorbed Pyridine and
gamma-MPS on Alumina Surface by Photoacoustic FT-IR
Spectroscopy

Final Technical Report was mailed to:

Dr. Robert Reeber
Department of the Army
U.S. Army Laboratory Command
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

Richard O. Ulsh
Chief, Information Processing Officer
Department of the Army
U.S. Army Laboratory Command
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

Commander
Defense Technical Information Center
Building 5 Cameron Station
ATTENTION: DDAC
Alexandria, VA 22314

Manager
Defense Logistics Studies
Information Exchange
ATTENTION: AMXMC-D
Fort Lee, VA 23801-6044

Commander
U.S. Army Tank-Automotive Command
ATTENTION: AMSTA-DDL
Warren, MI 48397-5000

Commander
U.S. Army Tank-Automotive Command
ATTENTION: AMSTA-CF
Warren, MI 48397-5000